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A review of the mathematical models for predicting the heating value of biomass materials

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ABSTRACT

Following the discovery of fire, biomass became the main source of energy used by mankind. Advanced societies have largely replaced the use of biomass with the use of fossil fuels, but our dependence on these ever scarcer resources, plus the need to reduce CO_2 emissions in the face of climate change, is forcing us to make use of renewable sources of energy, including biomass. The exploitation of this resource often requires that its heating value be known. This can be determined either directly (though not cheaply) or by the use of models that predict it using a number of easily and economically determined variables. The present review gathers together the most recent models for predicting the heating value of biomass, assesses their areas of application, and highlights errors that have been made in their formulation, transcription, and in the references made to them. Different models have relied upon elemental, proximal, structural, physical and chemical analyses to determine the values of necessary variables, although those relying on the results of the first two types of analysis have been the most popular. The simplest models and those with the widest range of applications are those most often referred to in the literature. The frequency with which important information has been left unconsidered in some studies, which has led to errors in the expressions presented, as well as errors of transcription and referencing, suggest that future work should be undertaken with greater diligence.

Contents

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1. Introduction

The term biomass broadly refers to organic matter, originated via a spontaneous or induced biological process, that can be used a source of energy. It is usually used to refer to certain types of wood, energy crops, marine algae, agricultural and silvicultural residues, and certain animal, industrial and human wastes [1,2]. In essence it is the solar energy chemically retained in plants and animals [1–5]. Some authors [6] distinguish between natural biomass and products derived from natural materials.

From a purely legal standpoint, biomass is understood as the biodegradable fraction of the biological products and residues of agricultural activities (including those of plant and animal origin), silvicultural activities, of the latters' associated industries (including fishing and aquaculture), and the biodegradable fraction of industrial and municipal waste [7].

The sustainable and rational use of this renewable energy resource [5,8,9] needs to be consolidated within national and supranational frameworks before fossil fuels become scarce [1,3,5,10–15]. Achieving this is all the more important given the uncertain future of nuclear energy. Despite our vast reserves of uranium and deuterium, the last of which could be used in nuclear fusion (though this technology is still in the research phase) [16], accidents such as those at Chernobyl and Fukushima have led to great concerns over safety.

In the European Union (EU), the clearest example of promoting energy efficiency and energy saving is the recent establishment of quotas that require 20% of all energy to be obtained from renewable resources by 2020 [7]. This goal has been adopted by all EU member states.

Currently, biomass provides only about 15–20% of global energy needs, although it is more important in developing nations where it may meet between one fifth and one third of energy demands [5,12,17]. It is particularly important in rural areas where it is commonly the most accessible and cheapest energy resource [18]. In most industrialised countries, biomass is much less important. For example, it has traditionally been used to meet only 5% of the energy needs of the EU and USA [1]. Some authors indicate that biomass is the best option for increasing our use of renewable energy [19–22]. Currently its direct combustion in furnaces is the most common way of generating heat and electricity from it [4,12,18,19,23,24], often in combination with coal owing to the technical, economic and environmental advantages this offers [25–27]. This, of course, precludes its conversion into some derived form of fuel [1,5,18,28,29].

A move away from fossil fuels is also required given the imperative need to reduce our emission of greenhouse gases [5,23,24,30,31]. It should be remembered that, although during combustion carbon reacts with oxygen to produce CO_2, the burning of recently produced biomass is a carbon neutral process; i.e., it produces no net increase in atmospheric CO_2. That which is released into the air only replaces that recently extracted from it during photosynthesis [1,3,5,13,18,32].

The use of biomass as a fuel in thermal and electrical applications, however, requires knowledge of its heating value (HV) [8–10,12,19,24]. The HV reflects the energy content of a fuel in a standardised fashion [19,24,33–37]. It is often expressed as the higher heating value (HHV) or lower heating value (LHV) [10]. The HHV, also known as the gross heating value (GHV), refers to the heat released by the complete combustion of a unit volume of fuel leading to the production of water vapour and its eventual condensation; the total energy released is measured at this point. The LHV, also known as the net heating value (NHV), does not contemplate this latent heat of water contained by fuels [24,32,36–38]. The values of HHV and LHV are usually expressed on the basis of dry weight (dry basis), or dry ash-free weight (dry ash-free basis [DAF]), since they can vary widely depending on the moisture content. Sometimes, however, these values are expressed on an "as received" basis [1,36–38].

The experimental or direct determination of the HV of a biomass using an adiabatic bomb calorimeter (to measure the change in enthalpy between the reactants and product) is burdensome [8–10,19,24,39]. The determination of its elemental – and especially its proximal – composition [19,23,24,40–43], followed by the calculation of the HV is a good alternative [10,44].Proximal analysis is used to determine the weight percentage of moisture, volatile material (VM), fixed carbon (FC) and ash in a biomass, while elemental analysis involves the determination, again in weight percentage, of C, H, N, O, S and, according to some authors, Cl [10,34,38,45–47]. Biomass can also be described in terms of its structural composition or its chemical and physical properties etc. [1,23,41].

There are many models for predicting the HHV of biomass that use the results of proximal and elemental analysis, as well as some that rely on the results of structural analysis or chemical or physical determinations [1,10,35,36,39,41]. The use of proximal analysis results has gained in importance over time among both researchers and engineers given the ease and speed with which such analysis can be accomplished [19,24,39,48,49].

Unfortunately, published models have traditionally suffered from a number of imprecisions, such as a failure to indicate the dry or fresh weight basis of the results, and failing to inform about the range of biomass types to which models can be applied [6,28,32,48].

The aim of the present work was (1) to review the classification, properties and uses of biomass, (2) to describe the methods available for analysing biomass, (3) to collect together the most recent models proposed for predicting the HHV or LHV of biomass, (4) to examine the applications of these models, and (5) to detect possible omissions, errors and imprecisions in the development, presentation of, and references made to, these models.

2. Classification, properties and use of biomass

2.1. Classification of biomass

In energy contexts, the term biomass is usually used to refer to plant materials [17], although it can have different origins [5], be of different composition, and have different properties [50]. Indeed, while the industrial use of biomass centres on the use of agricultural and silvicultural wastes, it also involves industrial and municipal wastes [51]. Given its diversity, a classification system is required that helps predict the behaviour of biomass [17]. Indeed, the lack of an accepted terminology and universal classification system has left the scientific literature full of misunderstandings and ambiguities [6].

Several classification systems have been proposed. One of the most simple is that of Demirbaş [52,53] who suggests the use of just three classification categories: wastes, forest products and energy crops. In contrast, Ni et al. [54] propose the use of four categories: energy crops, agricultural and livestock wastes, forest wastes, and municipal wastes. Taking into account recent advances [29,33], Khan et al. [17] proposed two new systems, one based on biomass origin, the other based on biomass properties:

(a) Based on origin
1. *Primary wastes*: The by-products of food crops and forestry products (cereal waste, wood waste etc.).
2. *Secondary wastes*: The by-products of biomass processing for the manufacture of food or other products (sawdust etc.).
3. *Tertiary wastes*: Biomass that has been used for some function but has reached the end of its useful life (e.g., wood used in construction etc.)
4. Energy crops.

(b) Based on properties (taking into account the arguments of Vassilev et al. [6]):
1. Wood and woody fuels (newly harvested hard- and softwoods).
2. Agricultural biomass (straw, grass, stalks, etc.).
3. Aquatic biomass (algae, etc.).
4. Animal and human wastes (bones, manure, etc.).
5. Contaminated biomass and industrial biomass (solid municipal wastes, waste-water treatment sludges, refuse-derived fuel, etc.).
6. Energy crops (i.e., crops grown for energy production purposes).
7. Biomass mixtures.

Other alternatives have also been proposed, such as that outlined in European standard CEN TC 335 for solid biofuels. The latter focuses on the origin of biofuels and proposes the categories of woody biomass (wood splinters, pellets, tree trunks, sawdust, etc.), herbaceous biomass, fruit and mixtures [17].

2.2. Biomass composition

Biomass includes cellulose, hemicellulose, lignin, lipids, simple sugars, starch, water, hydrocarbons, ash and other components [5]. The concentration of each class of compounds varies depending on the type of tissue involved, the phase of growth in which it was collected, and the conditions under which growth occurred. Owing to its carbohydrate content, biomass contains much more oxygen than do fossil fuels [17].

In terms of its elemental composition, and with particular reference to its C, H and O contents, biomass of different origin and type is rather similar. In general, the C content makes up around 30–60%, H some 5–6%, and O some 30–45% (wt% on dry basis). It usually also contains small amounts of N, S and Cl, generally accounting for <1% of its dry weight. With respect to coal, biomass usually has more O, Si, Cl and K (and sometimes more Ca), and less C, Al, Fe, Ti and S [3,5,17]. Some studies have reported correlations between variables determined in different types of analysis. For example, the lignin content correlates positively with the FC content [55].

2.3. Major properties and potential of biomass fuels

Biomass is currently thought to be the renewable energy source of greatest potential [56–58]. The annual production of biomass is some eight times that of all other types of energy source put together [59]. It is the only source of renewable C and can be directly converted into a liquid fuel [21]. Some authors [6,60] indicate, however, that the use of biomass fuels needs to be correctly managed.

There have been many attempts to predict the production of biomass [61,62], including the development of mathematical models to estimate forest biomass [63] and the amount of agricultural waste generated in, e.g., pruning, in this case taking into account variables such as the architecture of the tree type in question, whether irrigation has been used, variety, and inter-plant and inter-row distances [64]. The logistics of bioenergy chains have also been carefully studied [65,66].

The properties of a fuel influence the choice of combustion technique. The most important characteristics of fuels can be determined by elemental and proximal analysis, by the direct analysis of its heating value, and the ash fusion point [17]. The results obtained will depend on the origin of the biomass, its conditioning, and any conversion treatment to which it may have been subjected, etc. [17].

In general, biomass is not an ideal fuel [52,67]. On the same basis of weight, it usually has an HV below that of coal, a consequence of its lower C and H and greater O concentrations [3,17]. Generally, the HHV of biomass on dry basis is some 14–23 $MJ\,kg^{-1}$ [10] (15–17 $MJ\,kg^{-1}$ for agricultural wastes and 18–19 $MJ\,kg^{-1}$ for woody materials [5]), similar to that of peat [68]. Some researchers have reported values for different types of biomass [69].

The precise determination of the HHV of a biomass is important for the design of industrial processes to extract its energy, and for setting the price that consumers will need to pay for that energy [70]. With few exceptions, however, the energy derived from fossil fuels is more expensive [52,59]. The production of biomass fuel from wastes at specialised sites may be quite profitable; such plants could charge disposal fees to farmers etc., as well as make money on the sale of the fuel they produce [71].

Much of the biomass produced in agricultural and silvicultural systems is not used for the production of energy given the difficulty of its extraction, manipulation and transport; ignorance of the possibilities of using biomass also prevents investment in its use [61,62,72]. Some authors have studied the effects of pruning on the generation of wastes [73], while other have examined the options available for the collection of such waste [74] with a view to deincentivise its destruction in the field (which precludes any chance of usefully extracting its energy or making any economic profit from it). In practice, the HHV of these types of fuel is not determined directly [75], partly because of the intrinsic problems surrounding such an approach (the results usually require correction) [76].

The apparent density of biomass, also known as the energy density, is only of the order of 10–40% of that of most fossil fuels [5]. This is responsible for some of the major drawbacks of biomass [77], e.g., its low HV, its variability in terms of quality, the difficulty in controlling its combustion, the need for frequent re-supplying, difficulties in its transport, and the large storage space necessary. The need to store seasonally available materials is also a major problem [14]. However, most of these drawbacks can be overcome by densification procedures, which render biomass suitable as an energy source in the residential, commercial and industrial setting [77].

Table 1
Biomass analysis methods.

Analysis	Analytical method	References
All variables (standardised method)	ASTM E870-82(2006)	[83]
Proximal analysis		
Moisture content	UNE-EN 14774-1:2010	[84]
	ASTM E871-82(2006)	[85]
Ash	UNE-EN 14775:2010	[86]
	ASTM D1102-84(2007)	[87]
	ASTM E830-87(2004)	[88]
Volatile materials	UNE-EN 15148:2010	[89]
	ASTM E872-82(2006)	[90]
	ASTM E897-88(2004)	[91]
Fixed carbon	By difference	
Elemental analysis		
Carbon (C)	UNE-CEN/TS 15104:2008 EX	[92]
	ASTM E777-08	[93]
Hydrogen (H)	UNE-CEN/TS 15104:2008 EX	[92]
	ASTM E777-08	[93]
Nitrogen (N)	UNE-CEN/TS 15104:2008 EX	[92]
	ASTM E778-08	[94]
Sulphur (S)	ASTM E775-87(2008)e1	[95]
Oxygen (O)	By difference	
Chlorine (Cl)	ASTM E776-87(2009)	[96]
Gross calorific value	UNE 164001:2005 EX; UNE 164001:2005 EX ERRATUM:2008	[97,98]
	ASTM D5865-10ae1	[99]
	ASTM E711-87(2004)	[100]
Sample preparation for analysis	UNE-CEN/TS 14780:2008 EX	[101]

The greatest disadvantage of biomass as a fuel, however, is its high moisture content, which is inversely correlated with its HV [5,6].

2.4. Obtaining energy from biomass

There are two types of process that produce energy from biomass: thermochemical and biochemical/biological [54,78,79]. The former includes direct combustion, pyrolysis, gasification and liquefaction [21,71,80,81]. Combustion is the most widely used method [56], being responsible for some 97% of the bioenergy obtained worldwide. It is particularly important in developing countries [5]. Combustion consists of oxidising the biomass with excess air, using the hot gases produced to generate vapour in heat exchangers, which, via the Rankin cycle, allows the production of electricity [71]. The residual heat may also be used [53], resulting in what is termed cogeneration. Combustion can be broken down into three phases: drying, pyrolysis and reduction, and the combustion of volatile gases. It is this last phase that generates the most heat—over 70% of the total [5]. The heat produced by combustion needs to be used to heat other things or to generate electricity; currently, its storage is not a viable option [56].

The majority of biomass energy generation plants use products that might be employed in ways preferential to direct combustion. It is recommendable that only true end wastes be used in energy generation, thus returning to the atmosphere as late as possible the fixed CO_2 they contain [72].

Some 64% of the energy provided by biomass comes from wood and forestry wastes, 24% from solid municipal wastes, 5% from agricultural wastes and 5% from landfill gas [53]. Only very small amounts of toxic emissions are produced—usually close to or below current detection limits [82].

3. Methods of analysing biomass

Table 1 shows the main methods of analysing biomass according to American Standard Testing Methods (ASTM) and European Committee for Standardisation (CEN, according to its French designation) criteria. Standard ASTM E870-82(2006) [83] contains the methods for the standardised proximal and elemental analysis of wood fuels and the determination of their HV. Each of these methods has its own independent standard to describe it.

3.1. Elemental analysis

The elemental composition of a biomass fuel is one its most important features. It is usually complex, with six major elements in the organic phase (C, H, N, S, Cl and O), and 10 in the inorganic phase (Si, Al, Ti, Fe, Ca, Mg, Na, K, S and P). The latter are important in the characterisation of the ash. Traces of heavy metals are also usually present [82]. The percentages of N, S and Cl provide an idea of the impact of the use of a biomass fuel, while the concentrations of C, H and O allow the HV and the theoretical ratio of combustion in thermoconversion systems to be determined [1,17,102].

3.1.1. Carbon, hydrogen and oxygen

The main components of solid biofuels are C, H and O. Both the C and H are oxidised during combustion via an exothermic reaction, resulting in the formation of CO_2 and H_2O [103].

Carbon is the basic element of organic chemistry and is used by all known living organisms. Its concentration is positively related to the HHV [8,9,45], thus explaining why wood has a greater HHV than herbaceous biomass [103].

Hydrogen plays an important role in all fuel combustion systems. The greater the H + C/O ratio of a fuel, the greater its HHV [104].

The determination of C and H is usually accomplished using the methods outlined in standard ASTM E777-08 [93], while the O content is usually established as the difference between the sum of the percentages of C, H, N, S and that of the ash [45]. Some authors include the generally scant Cl content with the C, H, N and S content [8,9]. In Spain, standard UNE-CEN/TS 15104:2008 EX is in force [92] for the determination of C, H and N. Usually, the C content of a biomass is in the range of 42–71%, H in the range of 3–11%, and N in the range of 16–49% (wt% DAF) [6].

3.1.2. Nitrogen

Analysis of the N concentration is particularly important in terms of environmental protection [45]. One of the greatest environmental impacts of burning biofuels is the production of NO_x [17,102,103]. Conifers and deciduous trees have the lowest N concentrations, while the biomasses with the highest contents are logging waste and herbaceous crops [103]. Normally, N values fluctuate between 0.1 and 12% (wt% DAF) [6]. The N content is usually determined following standard ASTM E778-08 [94], although in Spain standard UNE-CEN/TS 15104:2008 EX may be used [92].

3.1.3. Sulphur

During combustion, the S in biomass fuels forms gaseous SO_2, sometimes SO_3, and alkalis [17,45,103]. However, biomass is usually poor in S [17] (around 0.01–2.3% [wt% DAF]) [6]. The S content is usually determined following the method outlined in standard ASTM E775-87(2008) [95], although some authors [2] refer to the use of standard ASTM D4239-11 [105].

3.1.4. Chlorine

The chlorine in biomass exerts its effects through its salts and the hydrochloric acid generated during combustion. These can have a negative impact on the walls of metallic furnaces. It is also forms acidic emissions and particles [3,17,45,106,107]. Its concentration differs from one type of biomass to another (generally between 0.01 and 0.9% [wt% DAF]) [6]. It is usually scarce in wood, and more abundant in straw, cereals, fat wastes, and fruit [17,45,103]. It has

been detected in large amounts in horticultural crops, especially tomatoes (*Solanum lycopersicum* L.) and beans (*Phaseoulus vulgaris* L.) [8,9]. Ash deposition can be a problem when concentrations of K, Si and Cl are high [3,17]. Chlorine is usually determined following the methods in standard ASTM E776-87(2009) [96].

3.1.5. Elemental ash

The major elements Al, Ca, Fe, K, Mg, Na, P, Si and Ti, and the minor elements As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn, along with Cl and S, can form ash. Knowing the ash content of a fuel is essential for the appropriate combustion method to be chosen [103]. Certain elements are found concentrated in specific biomass products, such as Si in olive pruning waste [108]. Fuels with low ash contents are preferable, such as wood, certain types of straw, fruit residues [103] and horticultural biomass [8,9]. Ash contents are determined following standards UNE-CEN/TS 14775:2007 EX [86], ASTM D1102-84(2007) [87] and ASTM E830-87(2004) [88]. However, its analysis is usually performed as part of proximal analysis (see below). As part of elemental analysis , some authors [18] refer to the use of standard ASTM D3682-01(2006), among others [109].

3.2. Proximal analysis

The aim of proximal analysis is to determine the weight percentage of VM, FC and ash [1,17]. The values of these variables have a bearing on biomass combustion. For example, a high ash content has been related to certain ignition and combustion problems, while a low dissolved ash fusion temperature can lead to furnace dirtying and the formation of slag. The HV increases with the FC and VM [1]. Contents are usually expressed on a dry weight basis after eliminating the moisture by drying (moisture levels can range between 10 and 70% even within plant biomass of a single type). The high moisture levels and oxygen content of biomass render its HV lower than that of other fuels, and can lead to problems of combustion [17,18,37,104,110]. When stored dry, the moisture level of biomass enters into equilibrium with that of its surroundings (around 20%) [3]. The methods for determining the moisture content are outlined in standards ASTM E871-82(2006) [85] and UNE-EN 14774-1:2010 [84].

3.2.1. Ash

Ash consists of the incombustible inorganic remnants of combustion. Some of these inorganic materials come from the biomass fuel itself, and some, e.g., soil particles, become incorporated during processing. These incorporated materials are usually in the majority [17].

The ash content of different plant biomass fuels differs, depending on the species, the age of the plant material used, the part of a plant used, and the level of contamination of the ground in which the plant grew. Nutrient availability, soil quality, the fertilisers used and weather conditions affect the content of K, Na, CL and P. Woody biomass generally has an appreciable amount of Ca and K, herbaceous biomass commonly has a high SI concentration, and in some cases, e.g., sunflower stalks, P levels can be high [1,3].

Ash contents vary from less than 1% (certain wood types) to up 30 or 40% (certain greenhouse crop wastes) (wt% on dry basis). Generally, a high ash content reduces the HV and requires some form of ash removal system be used [17,37,104,110].

Wood ash contents are determined following the methods of standard ASTM D1102-84(2007) [87], while waste-derived fuel ash contents are determined following ASTM E830-87(2004) [88] and, in Spain, UNE-CEN/TS 14775:2007 EX [86].

3.2.2. Volatile material

Biomass usually has a high VM content (48–86 wt% on dry basis) [5,6,17]. This VM is divided into light hydrocarbons, CO, CO_2, H, moisture and tars. A high VM content means biomass can ignite even at relatively low temperatures. However, this fraction is rapidly lost, and high temperatures need to be maintained for a long time if combustion is to be completed and emission levels are to be controlled [17]. The methods for determining the VM of wood and refuse-derived fuel are outlined in standards ASTM E872-82(2006) [90] and ASTM E897-88(2004) [91], while those for sold biomass fuels are outlined in UNE-CEN/TS 15148:2008 EX [92].

3.2.3. Fixed carbon

The FC content is calculated as the difference between 100% and the sum of the VM and ash (dry wt%) [45]. Its value generally falls in the range of 1–38 wt% on dry basis [6].

3.3. Structural analysis

Plant biomass contains a variable quantity of cellulose, hemicellulose and lignin (the main components [5,41]), and small quantities of lipids, proteins, simple sugars and starch. It also has inorganic constituents and water [1,3]. Cellulose, hemicellulose and lignin, in combination known as lignocellulose, makes up some 50% of the material produced by photosynthesis, and is the most abundant renewable organic resource on Earth.

The three components of lignocellulose are strongly linked by covalent bonds and networks [1]. Cellulose is the most abundant member of the trio, followed by hemicellulose and lignin. The first two compounds are macromolecules formed from sugars, while lignin is an aromatic polymer [1].

The structural analysis of a biomass is particularly important when trying to produce derived fuels and chemical products, as well as in the study of its combustion. It may also be useful in the determination of the HHV [1].

3.3.1. Cellulose and hemicellulose

Cellulose and hemicellulose are generally more abundant in hardwoods than softwoods. Hardwoods also have a greater proportion of extractives (see Section 3.3.3) that can increase the HV [41]; the energy content of the latter ($35\,MJ\,kg^{-1}$) is much greater than that of cellulose or hemicellulose (around $18\,MJ\,kg^{-1}$) [41,111]. Some authors indicate there to be no relationship between the HHV and the cellulose + hemicellulose content of lignocellulose fuels [112].

3.3.2. Lignin

Softwoods generally have a greater lignin content than hardwoods [41]. A positive correlation has been found between the lignin content of lignocellulose fuels and their HHV [3,112]. The energy content of lignin is about $26\,MJ\,kg^{-1}$ [41,111].

3.3.3. Extractives and ash

Wood contains certain extractive compounds such as fatty acids, resinous acids, tannins, sugars, terpene oligomers, sterols and hydrocarbons, etc., as well as ash [41]. At around $35\,MJ\,kg^{-1}$, wood extracts contain about twice the energy of cellulose or hemicellulose [41,111]; the content of these extractives is therefore important in the context of energy production.

3.4. Analysis of physical properties

The physical properties of different types of biomass vary enormously. The density, porosity, friability and internal surface area depends on the species in question, while the apparent density,

particle size and shape distribution are more dependent on the processing methods used [17].

4. Mathematical models for predicting the HHV or LHV of biomass

4.1. Models based on elemental analysis

Many formulae have been proposed for calculating the HHV from the results provided by elemental analysis [42]. In 1880, Dulong provided the first model for calculating the HV of coal samples [48,113], which involved the linear combination of the ash-free dry weight percentages of C, H, O and S [114]. Strache and Lant (in 1924) [115], Steuer (in 1926) [116], Vondracek (in 1927) [117], D'Huart (in 1930) [118], Schuster (in 1931) [119,120], Grummel and Davis (in 1933) [121], Seyler (in 1938) [122], Gumz (in 1938) [123], Sumegi (in 1939) [124], Mott and Spooner (in 1940) [113], Boie (in 1953) [125], along with others such as Dulong-Berthelot [126,127], Scheurer-Kestner [128–130] and Ruyter [131], have proposed variations of the Dulong model, including new coefficients and even new expressions.

At the end of the 1970s, the Institute for Gas Technology (IGT) [132] developed a new model that included the proportion of ash, while in the early 1980s Lloyd–Davenport [133] and Francis and Lloyd [134] included the S content in their models.

Generally, these models were developed through research on coal samples; their applicability, therefore, did not extend beyond this type of fuel. However, some authors have recently reported that the models of Boie are applicable to other forms of biomass [32,35,48,135]. In 1985 [136] Ebeling and Jenkins indicated the same for the IGT model. Kathiravale et al. [48] also indicated the models of Mott and Spooner, Vondracek, Secheurer-Kestner, Steuer and Ruyter, as well as a modification of the Dulong formula, to be applicable to municipal wastes and refuse. Some authors also suggest one of these is applicable for determining the HHV of agricultural wastes [137].

In 1972, Wilson [138] formulated an expression specifically for use with municipal wastes which differentiated between organic and inorganic C. This has been represented with slight differences in different publications [32,35,42,48,139].

In 1979, Chang [140] and Hazome et al. [141] published two new linear equations for use with domestic refuse, with Chang including the effect of Cl. The equations of Wilson, Chang and Boie were erroneously assigned by Arin and Demirbaş [41], Demirbaş and Demirbaş [37] and Hernández Moreno [139] to Corbitt, perhaps because of their inclusion in a book published by the latter author in 1989 [129].

The first equations that were derived from research with biomass were published in 1978 by Tillman [142]. Two of these equations (the second derived from the first) were linear functions in which the linear variable was the dry weight percentage of C; one was for use with wood and bark, the other with biomass in general. Both have been amply cited in the literature [1,10,35,41,139], although some authors fail to mention that they are expressed on dry basis [1,41,139] and make use of non-SI units [41,139].

In a doctoral thesis defended in 1980, Jenkins [143] proposed a model that took into account C, H, O and S, although it has been little cited. However, this author's later research with Ebeling [136,144] led to the proposal in 1985 of a series of models applicable to specific types of biomass, plus one of more general use. The latter has been cited on several occasions [10,24,35]. Beckman et al. [145] focused their efforts on fine-tuning a method for the determination of the HHV of biomass-derived oils, although their work has been little referenced by other authors [35].

In 1997, Demirbaş et al. [46] published two models, one for use with the hydropyrolytic oils of poplar trees that took into account C, H and O on the basis of ash-free percentage dry weight, and one for use with lignocellulose materials which took into account also the weight percentage of N on DAF basis. However, this paper contained an error in the naming of the table containing the elemental analysis results, referring to it as reflecting the results of proximal analysis. In addition, in this table the authors express the results in terms of percentage dry weight and not percentage ash-free dry weight as earlier described. When the expressions are examined using the data provided, the conclusion is reached that they should indeed have been expressed in terms of percentage dry weight. Further, it would appear that both expressions lack the term $\times 10^{-2}$ that Demirbaş himself included when he made use of these equations in further publications in the same year [40] and in 2004 [18] (although in neither case did the author clarify whether they were based on percentage dry weight or ash-free percentage dry weight). The lignocellulose model of Demirbaş has been cited on many occasions [24,139,146–148], although almost always without the opportune corrections. In some cases it has even appeared with a surprising modification of the N coefficient [37,41,139] or the suppression of the values for O and N [36], coinciding with the equation proposed by Demirbaş for diesel fuel [148]. More recently it has been cited with further errors and incorrectly referenced [1]. In his 1997 paper, Demirbaş et al. [46] also included two expressions for calculating the LHV of lignocellulose materials. These took into account the moisture content of samples but did not cite the variables to be considered in its calculation. Interest in these last two equations has been scant.

In 1995, Niessen [149] published an equation applicable to waste-water sludges, although it has received little attention. Some years later, Meraz et al. [75] and Kathiravale et al. [48] both proposed two models, one applicable to wastes in general and one to solid municipal wastes. But again, little interest was shown in them. The equation proposed by Meraz et al. includes a correction for the moisture content. Results would appear to be expressed on "as received" basis (although this is not made clear); the HHV is expressed as a negative value. However, other authors using this model have removed the inclusion of the moisture content, and presented the HHV results with a positive sign [147]. In their work, Kathiravale et al. [48] failed to report the values of the variables used in the development of their model.

In 2004, Demirbaş and Demirbaş [37] produced four new models based on the results of elemental analysis, two involving the results for the C content, and two involving the sum of C + H. Unfortunately, these authors did not specify whether their values were expressed on dry basis or DAF basis, although the former appears to be more likely.

In 2005, Friedl et al. [32] proposed a quadratic equation involving three variables, C, H and N (Table 2), for use with biomass materials. In fact this equation represents the mean of two models examined in the same paper. Yin [10] underscored the importance of this equation.

Sheng and Azevedo [24] reported a series of models, two of which were based on the results of elemental analysis. One of these is a linear function of the concentration of C, while the other takes into account the variables C, H and O. It should be noted that, in this model, the O can only be interpreted as the sum of O plus S, N and Cl in the organic material, since it is calculated as that remaining once the C, H and ash is eliminated. Again, Yin [10] recognised the advances provided by this work, while at the same time proposing a new model obtained from research into a wide range of materials.

In 2005, Thipkhunthod et al. [147] reviewed many of the published models and used five as the basis for obtaining others, with new, simply obtained coefficients, that could be used with waste-water sludges.

Finally Callejón-Ferre et al. [8,9] studied the energy potential of intensive horticulture wastes produced in greenhouse in the

Table 2
Recent models based on elemental analysis.

Researcher	Correlation (HHV, MJ kg^{-1} dry basis)	Biomass types	Publication year	References	Comments
Tillman	HHV = 0.4373[C] − 0.3059[a]	Wood and wood bark	1978	[142]	References with errors
	HHV = 0.4373[C] − 1.6701 (modification of the above)	Whole range of biomass materials			References with errors
Jenkins	HHV = 0.4791[C] + 0.6676[H] + 0.589[O] + 1.2077[S] − 8.42	Residue-derived fuels	1980	[143]	
Jenkins and Ebeling	HHV = 3.754 + 0.322[C]	Field crops	1985	[136,144]	No SE
	HHV = 12.963 + 0.131[C]	Vineyard prunings			No SE
	HHV = 1.209 + 0.379[C]	Food and fibre processing wastes			No SE
	HHV = 3.210 + 0.3333[C]	Hulls and shells			No SE
	HHV = 0.093 + 0.398[C]	Forest residues			No SE
	HHV = 2.491 + 0.347[C]	Energy crops			No SE
	HHV = 5.205 + 0.293[C]	Wood			No SE
	HHV = 3.754 + 0.322[C]	All biomass			No SE
	HHV = −4.320 + 0.375[C] − 2.383[H] + 0.438[O]	Field crops			Not $R^2_{ajusted}$, No SE
	HHV = −27.805 + 0.685[C] − 0.705[H] + 0.433[O]	Vineyard prunings			Not $R^2_{ajusted}$, No SE
	HHV = −5.501 + 0.317[C] + 0.998[H] + 0.109[O]	Food and fibre processing wastes			Not $R^2_{ajusted}$, No SE
	HHV = 0.007 + 0.311[C] + 0.752[H] + 0.006[O]	Hulls and shells			Not $R^2_{ajusted}$, No SE
	HHV = −0.049 + 0.332[C] + 0.851[H] − 0.036[O]	Forest residues			Not $R^2_{ajusted}$, No SE
	HHV = −1.005 + 0.348[C] − 1.073[H] + 0.222[O]	Energy crops			Not $R^2_{ajusted}$, No SE
	HHV = 1.177 + 0.306[C] + 0.703[H] − 0.016[O]	Wood			Not $R^2_{ajusted}$, No SE
	HHV = −0.763 + 0.301[C] + 0.525[H] + 0.064[O]	All biomass			Not $R^2_{ajusted}$, No SE
Beckman et al.	HHV = 0.352[C] + 0.944[H] + 0.105[S–O]	Biomass-derived oils	1990	[145]	
Demirbaş et al.	HHV* = (33.5[C*] + 142.3[H*] − 15.4[O*]) × 10^{-2}	Hydropyrolytic oils from poplar wood	1997	[46]	Not $R^2_{ajusted}$, No SE
	HHV* = (33.5[C*] + 142.3[H*] − 15.4[O*] − 14.5[N*]) × 10^{-2}	Olive husks, wheat straw, corn cobs, charcoal from olives husks, wheat straw and pine cones, pyrolytic oil from olive husks, wheat straw and pine cones			Not $R^2_{ajusted}$, No SE Fixed error References with errors
Niessen	HHV* = 0.2322[C*] + 0.7655[H*] − 0.072[O*] − 0.0419[N*] + 0.0698[S*] + 0.0262[Cl*] + 0.1814[P*]	Waste-water sludges	1995	[149]	
Meraz et al.	HHV = (1 − H_2O/100)·(−0.3708[C] − 1.1124[H] + 0.1391[O] − 0.3178[N] − 0.1391[S])	Paper and paper products; food and food waste: citrus rinds and seeds, food waste, fried fats, meat scraps (cooked), mixed garbage and vegetable food waste; trees, wood, brush and plants: balsam spruce, brush, construction softwood, evergreen shrubs, flowering plants, furniture wood, grass, soil, leaves, green logs, lawn grass, mixed greens, other organic material, ripe leaves, rotten timber, rubber, leather, and hard plastics, waste hardwood, wood, wood and bark, wood and textiles, yard waste), domestic wastes, refuse-derived fuels, prepared solid waste incinerator samples, other wastes	2003	[75]	Not $R^2_{ajusted}$ Basis (dry basis, DAF basis etc.) unsure
Kathiravale et al.	HHV = 0.416638[C] − 0.570017[H] + 0.259031[O] + 0.598955[N] − 5.829078	Municipal solid waste	2003	[48]	Not $R^2_{ajusted}$, No SE Unpublished data
Demirbaş and Demirbaş	HHV = 0.4084[C] − 0.459	Cellulose, hardwood lignin, softwood lignin, beech wood, spruce wood, yellow pine, poplar wood, pine bark, wood pyrolytic oil, wood charcoal, cotton stalks, rice hulls, grass, hazelnut shells, walnut shells, olive husks, corn cobs, wheat straw, corn stover, sugarcane bagasse and pine needles	2004	[37]	Not R^2, No SE
	HHV = 0.3699[C] − 1.3178				Not R^2, No SE
	HHV = 0.4181[C+H] − 3.4085				Not $R^2_{ajusted}$, No SE
	HHV = 0.3856[C+H] − 1.6938				Not $R^2_{ajusted}$, No SE Basis (dry basis, DAF basis, etc.) unsure

Table 2 (*Continued*)

Researcher	Correlation (HHV, $MJ\,kg^{-1}$ dry basis)	Biomass types	Publication year	References	Comments
Friedl et al.	$HHV = 0.00355[C]^2 - 0.232[C] - 2.230[H] + 0.0512[C{\cdot}H] + 0.131[N] + 20.600$	*Miscanthus* energy grass, other energy grass, wood material, wood waste, cereals, millet, sunflower, hemp, waste, other plant material, other non-plant material	2005	[32]	Not $R^2_{ajusted}$
Sheng and Azevedo	$HHV = 0.3259[C] + 3.4597$	Wide range of biomass materials	2005	[24]	
	$HHV = -1.3675 + 0.3137[C] + 0.7009[H] + 0.0318[O']$[b]				Not $R^2_{ajusted}$
Thipkhunthod et al.	$HHV = 0.4912[C] - 0.9119[H] + 0.1177[O]$	Sewage sludge	2005	[147]	Not $R^2_{ajusted}$
	$HHV = 0.4925[C] - 0.9260[H] + 0.1176[O] + 0.0193[S]$				Not $R^2_{ajusted}$
	$HHV = 0.4148[C] - 0.1841[H] + 0.1789[O] - 2.1595$				Not $R^2_{ajusted}$
	$HHV = 0.4259[C] - 0.0698[H] + 0.1817[O] - 0.1805[N] - 2.2770$				Not $R^2_{ajusted}$
	$HHV = 0.4302[C] - 0.1867[H] - 0.1274[N] + 0.1786[S] + 0.1842[O] - 2.3799$				Not $R^2_{ajusted}$
Yin	$HHV = 0.2949[C] + 0.8250[H]$	Pistachio soft shells, coconut shells, wheat straw, rice husks, sugarcane bagasse, bamboo wood, olive stones, almond shells, sunflower seed shells, esparto plants, shea meal, cotton stalks, peanut shells, hazelnut shells, wet grains, corn stover, coffee husks, sugar cane straw, *marabú, soplillo*, *Casuarina equisetifolia* leaf, *Lantana camara* leaf, oil palm fruit bunches, olive kernels, olive kernel shells, olive cake, forest residues, cotton residues, alfalfa stems, rice straw, switch grass, willow wood, hybrid poplar, almond hulls, oak wood (small branch), oak wood (medium branch), oak wood (large branch), pine chips, corn straw, rape straw, palm kernels, B-wood, pepper plant, biomass mix, *ipil ipil*, olive pits, pistachio shells.	2011	[10]	
Callejón-Ferre et al.	$HHV = -3.147 + 0.468[C]$	Greenhouse crop residues: courgette (*Cucurbita pepo* L.), cucumber (*Cucumis sativus* L.), aubergine (*Solanum melongena* L.), tomato (*Solanum lycopersicum* L.), bean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), water melon (*Citrillus vulgaris* Schrad.) and melon (*Cucumis melo* L.).	2011	[8,9]	
	$HHV = -2.907 + 0.491[C] + 0.261[H]$				
	$HHV = -3.393 + 0.507[C] - 0.341[H] + 0.067[N]$				
	$HHV = -3.440 + 0.517[C{+}N] - 0.433[H{+}N]$				
	$HHV = 5.736 + 0.006[C]^2$				
	$HHV = -5.290 + 0.493[C] + 5.052[H]^{-1}$				

C: carbon (wt% dry basis); H: hydrogen (wt% dry basis); N: nitrogen (wt% dry basis); S: sulphur (wt% dry basis); Cl: chlorine (wt% dry basis); O: oxygen (wt% dry basis), P: phosphorous (wt% dry basis); * indicates composition on dry ash free basis (DAF basis); No SE: no study of errors; Not R^2: lack of R^2 in univariate model; Not $R^2_{ajusted}$: lack of $R^2_{ajusted}$ in multivariate model.

[a] Correlations converted to $Mj\,kg^{-1}$ using the following conversion factor: $1\ Btu\,lb^{-1} = 2.3261 \times 10^{-3}\ Mj\,kg^{-1}$.

[b] Here O′ is the sum of the contents of oxygen and other elements (including S, N, Cl, etc.) in the organic matter, i.e., O′ = 100-C–H–Ash.

Province of Almería (Spain). The area has one of the highest concentration of greenhouses in the world [150], and produces huge crops of courgettes (*Cucurbita pepo* L.), cucumbers (*Cucumis sativus* L.), aubergines (*Solanum melongena* L.), tomatoes (*S. lycopersicum* L.), beans (*P. vulgaris* L.), peppers (*Capsicum annuum* L.), water melons (*Citrillus vulgaris* Schrad.), and melons (*Cucumis melo* L.) etc. [151]. This research required the fine tuning of models for predicting the characteristics of this type of biomass; four models using the results of elemental analysis were finally proposed.

4.2. Models based on proximal analysis

The models based on proximal analysis, i.e., which take into account FC, VM and ash, have historically received less attention, perhaps because of the greater accuracy of models based on elemental analysis when used with coal. However, some models have achieved notable importance, e.g., that proposed by Goutal at the beginning of the 20th century [152] for coal (although some authors have used it for domestic refuse [48]). The Goutal model provides the HHV as a function of the FC and VM (DAF basis); the second only takes into account the VM. Other models have been proposed, such as the Bento model and the Traditional model [128]; these have sometimes been used with domestic refuse [48,130]. In the 1950s the model of Schuster [153] also achieved some recognition.

Recently, models based on the results of proximal analysis have enjoyed a certain comeback. They have been used with both coal [154,155] and biomass [136,156]. Ebeling and Jenkins [136] proposed another 16 models based on the results of proximal analysis, indicating those involving the variable 'ash content' on its own to be the most important given the great ease with which its value can be determined. Unfortunately, these models were not recognised to the extent they may deserve.

Jiménez and González [156] proposed a very simple formula for estimating the HHV from the sum of the concentrations of VM and FC. Although they did not so indicate, it can be inferred that results are expressed on dry basis. This model awakened the interest of other researchers who made reference to them in their works [10,12,24,39,155], although in some cases the units appear to be confused [49]. One of the two models proposed by Demirbaş in 1997 [40] was incorrectly assigned [28] to the Jiménez and González. The latter Demirbaş models make use of the guidelines set out by Goutal. They have been cited many times [1,4,18,24,36,37,39,41,49,104,139,146,157].

In 2001, Cordero et al. [12] proposed two models that were really just two ways of expressing the same idea. These equations have been taken into account in later works [10,28,39,155], but sometimes with errors of transcription [1,49].

Two years later Demirbaş [110] presented two quadratic equations relating FC and VM respectively with the HHV, expressed on a dry ash/extractive-free basis. Table 3 shows these models but after having corrected the coefficient used to multiply $[FC^*]^2$ since, given the data provided, this must have been incorrectly written. The only two references to these models continue in this error [41,139].

In 2003, Kathiravale et al. [48] proposed two equations for use with solid municipal wastes, although they did not provide the values from which they were developed. Two years later, Sheng and Azevedo [24] were guilty of the same when proposing two equations for general use with biomass. Nonetheless, a number of authors have cited their work [1,10,39].

Parik et al. [49] proposed an equation involving the FC, VM and ash. Although their results and conclusions are justified given the data they used, the model is mathematically questionable since the FC is derived from the VM and ash contents. A number of other authors have cited these models [10,28,38,39,155].

In work to update existing models for use with waste-water sludge, Thipkhunthod et al. [147] proposed five equations based on the results of proximal analysis. Later, Huang [39], who worked with a large number of straw samples, proposed two models (one linear, one non-linear) in which the only variable required to be known was the ash content. Although this author did not report the data used to develop the model, the work involved the use of artificial neural networks (ANN), a method earlier used by Patel et al. [38]. The complexity of this model has, however, reduced its practical use [156].

In 2009, Demirbaş [43] proposed a new equation for determining the HHV of biomass, this time on a DAF basis.

In 2010, and having studied a wide range of biomass types, Erol et al. [19] proposed three models for calculating the NHV. These involved the use of FC, VM and ash (once again a mathematically questionable approach since the values of these variables are inter-related). These equations have been little cited (perhaps because of their recent publication date), but again in an erroneous fashion [1].

In 2011, Yin [10] proposed a new, easily used model for determining the HHV employing the results of proximal analysis. Given its recent publication it has been little cited in the literature.

Finally, of the 20 models reported by Callejón-Ferre et al. [8,9] for use with agricultural waste produced in Almería, three require only the results of proximal analysis. Two of these models involve linear functions of one variable (ash or VM), and one requires the use of two variables (ash and VM).

4.3. Models based on elemental and proximal analysis

Some models use the results of both elemental and proximal analysis (Table 4). The oldest, proposed by Grabosky and Bain in 1981 [126], was later cited by Sheng and Azevedo [24] and by Channiwala and Parikh [35]. The latter authors produced a single model for use with solids, liquids and gases. This wide range of use may explain its citing in later works by other authors [10,24], although some have made errors in its transcription [38].

In 2005, Thipkhunthod et al. [147] proposed nine models derived from equations published by other authors.

The models of Callejón-Ferre et al. [8,9] are the latest to expand the list of those that take the results of elemental plus proximal analysis into account.

4.4. Models based on the results of structural analysis

Some models for calculating the HHV are based on their results of structural analysis (Table 5). These take into account the cellulose + hemicellulose (i.e., holocellulose) and lignin contents, and sometimes the effect of extractives. Shafizadeh and Degroot [158] pioneered this type of model, taking into account all of these variables. Several authors have cited them [12,156], but sometimes making changes to them without explaining why [24].

In 1978, Tillman [142] used just one variable in a model to determine the HHV of wood (expressed both on a dry weight and DAF basis). Although some authors have failed to transcribe the equation without errors [1,24], Jiménez and González [156], White [111], Arin and Demirbaş [41] and Hernández Moreno [139] have used it as the basis of their investigations. Even so, the first of these make use of unusual units, and the remainder use non-SI units. In some cases [41,139] these equations were even grouped with those involving the results of elemental analysis, perhaps due to an erroneous interpretation of the abbreviation used by White to refer to cellulose + hemicellulose.

In 1984, White [111] proposed four equations, one applicable to wood containing extractives, the other to three different types of wood free of extractives. White also proposed a fifth equation based on that of Tillman [142].

Table 3
Recent models based on proximate analysis.

Researcher	Correlation (HHV, MJ kg^{-1} dry basis)	Biomass types	Publication year	References	Comments
Jenkins and Ebeling	HHV = 19.246 − 0.196[Ash]	Field crops	1985	[136,144]	No SE
	HHV = 19.830 − 0.277[Ash]	Vineyard prunings			No SE
	HHV = 21.043 − 0.282[Ash]	Food and fibre processing wastes			No SE
	HHV = 20.353 − 0.234[Ash]	Hulls and shells			No SE
	HHV = 20.179 − 0.365[Ash]	Forest residues			No SE
	HHV = 19.610 − 0.242[Ash]	Energy crops			No SE
	HHV = 20.060 − 0.352[Ash]	Wood			No SE
	HHV = 20.067 − 2.196[Ash]	All biomass			No SE
	HHV = 21.439 − 0.217[Ash] − 0.028[VM]	Field crops			Not $R^2_{ajusted}$, No SE
	HHV = 32.574 − 0.443[Ash] − 0.159[VM]	Vineyard prunings			Not $R^2_{ajusted}$, No SE
	HHV = 27.013 − 0.335[Ash] − 0.077[VM]	Food and fibre processing wastes			Not $R^2_{ajusted}$, No SE
	HHV = 27.239 − 0.306[Ash] − 0.089[VM]	Hulls and shells			Not $R^2_{ajusted}$, No SE
	HHV = 22.608 − 0.409[Ash] − 0.030[VM]	Forest residues			Not $R^2_{ajusted}$, No SE
	HHV = 25.235 − 0.328[Ash] − 0.068[VM]	Energy crops			Not $R^2_{ajusted}$, No SE
	HHV = 23.885 − 0.430[Ash] − 0.047[VM]	Wood			Not $R^2_{ajusted}$, No SE
	HHV = 26.601 − 0.304[Ash] − 0.082[VM]	All biomass			Not $R^2_{ajusted}$, No SE
Jiménez and González	HHV = −10.81408 + 0.3133[VM + FC]	Wheat straw, olive twigs, olive wood, vine shoots, sunflower stalks, cotton plant stalks, sunflower seed husks, olive stones, olive marc, holm oak residues, eucalyptus residues	1991	[156]	Not $R^2_{ajusted}$, No SE Basis (dry basis, DAF basis, etc.) unsure References with errors
Demirbaş	HHV = 0.196[FC] + 14.119 HHV = 0.312[FC] + 0.1534[VM]	Olive husks, hazelnut shells, hazelnut seedcoats, softwoods, hardwoods, wheat straw, wood bark, waste material, corn cobs, tea waste, corn stover, spruce wood, beech wood, tobacco leaf, *Ailanthus* wood and tobacco stalks	1997	[40]	No SE Not $R^2_{ajusted}$, No SE Basis (dry basis, DAF basis, etc.) unsure References with errors
Cordero et al.	HHV = 0.3543[FC] + 0.1708[VM] HHV = 35.430 + 0.1835[VM] − 0.3543[Ash]	Forest wastes including sawdust from oak, *Pinus* and eucalyptus species (*Quercus rotundifolia*, *Pinus halepensis*, *Eucalyptus saligna*), and agricultural wastes (olive stones, almond shells and wet straw)	2001	[12]	Not $R^2_{ajusted}$, No SE Not $R^2_{ajusted}$, No SE References with errors
Demirbaş	HHV** = −0.0066[FC**]^2 + 0.5866[FC**] + 8.752 HHV** = −0.0066[VM**]^2 + 0.7371[VM**] + 1.2305	Sunflower shell, almond shell, hazelnut shells, wood bark, olive husks, hazelnut kernel husks, walnut shells	2003	[110]	No SE Fixed error No SE
Kathiravale et al.	HHV = 0.356248[VM] − 6.998497 HHV = 0.356047[VM] − 0.119035[FC] − 5.600613	Municipal solid waste	2003	[48]	No SE Not $R^2_{ajusted}$, No SE Unpublished data
Sheng and Azevedo	HHV = 19.914 − 0.2324[Ash] HHV = −3.0368 + 0.2218[VM] + 0.2601[FC]	Wide range of biomass materials	2005	[24]	 Not $R^2_{ajusted}$ Unpublished data

Table 3 (*Continued*)

Researcher	Correlation (HHV, $MJ\,kg^{-1}$ dry basis)	Biomass types	Publication year	References	Comments
Parikh et al.	HHV = 0.3536[FC] + 0.1559[VM] – 0.0078[Ash]	Coals/coke; manufactured fuel/wood (cotton shell briquettes, Lantana briquettes, pressed mud briquettes, block wood, plywood); biomass—pits/shells/seeds/cobs (peach pit, macadamia shells, pistachio shells, hazelnut shells, coconut shell powder, cotton shells, spearmint, corn cobs, corn stover, corn cob); biomass—wood/energy crops (wood chips, canyon live oak, red wood, softwood, spruce wood, pine wood, subabul wood, eucalyptus, *Eucalyptus grandis*, Sudan grass), other biomass—barks/prunings (Douglas fir, loblolly pine, eucalyptus bark, almond, Cabernet Sauvignon wood, walnut, olive twigs, wood chips, coffee chaff, tapero root skin scale scrapping), other biomass—straws (wheat straw, paddy straw, rice straw, coconut stem); other biomass-stalks (cotton stalk, mustard stalk, eucalyptus stalk, mulberry stick), other biomass-fibrous material/leaves/grass (coconut coir, bagasse, bagasse pith, sweet sorghum bagasse, moringa-olifera leaves, sena leaves, sugar cane leaves, olive marc, miscalthus, del lake weed, tea bush), other biomass—hulls/husk/dust (sal seed husks, bamboo dust, eucalyptus sawdust, sawdust, sawdust + mustard), other biomass—others/misc. (*Mentha piperita*, *Grewia optiva*, water hyacinth, cecer cones), biomass waste material (tea waste, bamboo stick waste, tannery waste, fly ash, pine needles, castor seed cake), biomass waste material—milling industry waste (cotton gin waste, cotton gin trash, Alabama oak wood waste, white fir, tan oak), biomass waste material—refuse/MSW (industrial waste, poultry pure waste, municipal solid waste), biomass chars (redwood char, oak char, coconut shell char, *Quercus rotundifolia*, *Pinus halepensis*, *Eucalyptus saligna*, rice husk char, rose apple char)	2005	[49]	Not $R^2_{ajusted}$ Relationship between variables
Thipkhunthod et al.	HHV = 0.25983([VM] + [FC]) – 2.45476	Sewage sludge	2005	[147]	Not $R^2_{ajusted}$
	HHV = 0.25575[VM] + 0.28388[FC] – 0.00276				Not $R^2_{ajusted}$
	HHV = 0.27807([VM] + [FC]) – 0.05044[M] – 2.87552[a]				Not $R^2_{ajusted}$
	HHV = 0.21998[VM] + 0.32744[FC] – 0.06839[a]				Not $R^2_{ajusted}$
	HHV = 0.27604[VM] + 0.28970[FC] – 0.05145[M] – 2.84753[a]				Not $R^2_{ajusted}$
Huang et al.	HHV = 18.96016 – 0.22527[Ash]	Rice straw and wheat straw	2008	[39]	
	HHV = 8765.42392 – 1029.38880[Ash] – 43824.25734$[Ash]^{-1}$ + 74.15588$[Ash]^2$ + 113019.57518$[Ash]^{-2}$ – 3.21628$[Ash]^3$ – 82925.42438$[Ash]^{-3}$ + 0.07708$[Ash]^4$ – 108635.32266$[Ash]^{-4}$ – 0.00078$[Ash]^5$ – 58745.73352$[Ash]^{-5}$				Unpublished data
Demirbaş	HHV* = –0.1882[VM*] + 32.94	Olive husks, hazelnut shells, hazelnut kernel husks, softwoods, hardwoods, wheat straw, wood bark, waste material, corn cobs, tea waste, corn stover, spruce wood, beech wood, tobacco leaf, *Ailanthus* wood, tobacco stalks	2009	[43]	Not R^2, No SE

Table 3 (*Continued*)

Researcher	Correlation (HHV, MJ kg^{-1} dry basis)	Biomass types	Publication year	References	Comments
Erol et al.	NHV = 15.2 + 0.192[FC]	Broad bean husks, sunflower shells, French bean stalks, sunflower stalks and stover, sourcheery stalks, walnut shells, almond shells, peanut shells, cornelian cheery stones, apricot stones, peach stones, apricot bagasse, peach bagasse, hybrid poplar, ash tree, pine cone, soybean cake, cotton cake, rapeseed, potato peel	2010	[19]	Not R^2
	NHV = 14.2 + 0.38[FC] − 0.00721[FC]^2				Not R^2_{ajusted}
	NHV = 14.4 + 0.382[FC] − 0.00758[FC]^2 + 0.0417[Ash]				Not R^2_{ajusted}
	NHV = 13.0 + 0.392[FC] − 0.00735[FC]^2 + 0.0231[Ash] + 0.0149[VM]				Not R^2_{ajusted}
	NHV = 13.8 + 0.402[FC] − 0.00833[FC]^2 + 0.742[Ash]$^{-1}$ + 0.0003[VM·Ash]				Not R^2_{ajusted}
	NHV = −5.9 + 0.836[FC] − 0.0116[FC]^2 + 0.00209[VM]^2 + 0.0325[Ash]^2				Not R^2_{ajusted}
	NHV = 46.4 − 1.19[VM + Ash] + 0.00409[VM]^2 + 0.0179[Ash]^2 − 0.0118[FC]^2 + 4634[OM]$^{-1}$ + 0.23[Ash]$^{-1}$				Not R^2_{ajusted}
	NHV = −116 − 133[Ash] − 0.005[VM] + 0.0179[Ash]^2 + 1.92[VM + Ash] − 0.0227[VM·Ash] − 0.0122[VM]^2 + 0.0299[Ash]^2 + 6133[OM]$^{-1}$ + 0.82[Ash]$^{-1}$				Not R^2_{ajusted}
	NHV = 11.6–0.226[FC] + 0.0371[VM] + 0.0206[Ash]^2				Not R^2_{ajusted}
	NHV = 7.1 − 0.23[FC] + 0.04[VM] + [OM] + 0.0072[Ash]^2				Not R^2_{ajusted}
	NHV = 356 − 3.2[FC] − 3.41[VM + Ash]				Not R^2_{ajusted}
	NHV = 34.4 − 0.226[VM + Ash] + 0.0356[VM] +0.00019[VM·Ash]				Not R^2_{ajusted}
	NHV = 18.2 − 0.137[FC] − 0.00031[VM]^2 − 0.0071[Ash]^2				Not R^2_{ajusted} Relationship between variables
Yin	HHV = 0.1905[VM] + 0.2521[FC]	Pistachio soft shells, coconut shells, wheat straw, rice husks, sugarcane bagasse, bamboo wood, olive stones, almond shells, sunflower seed shells, esparto plant, shea meal, cotton stalks, peanut shells, hazelnut shells, dried grains, wet grains, corn stover, coffee husks, sugar cane straw, *marabú*, *soplillo*, *Casuarina equisetifolia* leaf, *Lantana camara* leaf, oil palm fruit bunches, olive kernels, olive kernel shells, olive cake, forest residue, cotton residue, alfalfa stems, rice straw, switch grass, willow wood, hybrid poplar, almond hulls, oak wood (small branch), oak wood (medium branch), oak wood (large branch), pine chips, corn straw, rape straw, palm kernels, B-wood, pepper plant, biomass mix, *ipil ipil*, olive pits, pistachio shells.	2011	[10]	
Callejón-Ferre et al.	HHV = 20.086 − 0.261[Ash]	Greenhouse crop residues: courgette (*Cucurbita pepo* L.), cucumber (*Cucumis sativus* L.), aubergine (*Solanum melongena* L.), tomato (*Solanum lycopersicum* L.), bean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), water melon (*Citrillus vulgaris* Schrad.) and melon (*Cucumis melo* L.).	2011	[8,9]	
	HHV = −13.173 + 0.416[VM]				
	HHV = −2.057 − 0.092[Ash] + 0.279[VM]				

FC: fixed carbon (wt% dry basis); VM: volatile matter (wt% dry basis); OM: organic matter (wt% dry basis); Ash (wt% dry basis); M: moisture (% by mass); *: on dry ash-free (DAF) basis; **: on ash/extractive-free basis; No SE: no study of errors; Not R^2: lack of R^2 in univariate model; Not R^2_{ajusted}: lack of R^2_{ajusted} in multivariate model.

[a] Composition in wt% on a air-dried basis.

Table 4
Recent models based on elemental and proximate analysis.

Researcher	Correlation (HHV, MJ kg^{-1} dry basis)	Biomass types	Publication year	References	Comments
Grabosky and Bain	$HHV = 0.328[C] + 1.4306[H] - 0.0237[N] + 0.0929[S] - (1 - [Ash]/100)(40.11[H]/[C])$	Wide range of biomass materials	1981	[126]	
Channiwala and Parikh	$HHV = 0.3491[C] + 1.1783[H] + 0.1005[S] - 0.1034[O] - 0.0151[N] - 0.0211[Ash]$	Gaseous fuels, liquid fuels, solid fuels: coal/coke, biomass material (peat, coconut shells, akhrot shells, groundnut shells, oak bark, western hemlock wood, Douglass fir wood, chaparral wood, eucalyptus wood, casuarina wood, bamboo wood, neem wood, mango wood, jujube wood, block wood, cotton stalks, bagasse, rice husks, subabul wood, plywood, saw dust, soquel point giant brown kelp, millet straw, wheat straw, jawar straw, rice straw, rice husks, rice straw bran, coconut coir pith, millet grain waste, cotton gin waste), refuse, animal waste etc. (MSW, sewage sludge, digested slurry, RDF, animal waste, chars, red wood char, MSW char, ERCO char, lignite char)	2002	[35]	Not $R^2_{ajusted}$ References with errors
Thipkhunthod et al.	$HHV = 0.4064[C] - 0.2106[H] + 0.1547[S] + 0.1603[O] - 0.1513N - 0.0238[Ash] + 0.0034$	Sewage sludge	2005	[147]	Not $R^2_{ajusted}$
	$HHV = 0.4064[C] - 0.2105[H] + 0.1548[S] + 0.1604[O] - 0.1512N - 0.0238[Ash]$				Not $R^2_{ajusted}$
	$HHV = 0.3959[C] - 0.4471[H] + 0.2555[S] + 0.1543([O] + [N]) - 0.0181[Ash] - 0.0217$				Not $R^2_{ajusted}$
	$HHV = 0.3956[C] - 0.4460[H] + 0.2545[S] + 0.1540([O] + [N]) - 0.0219[Ash]$				Not $R^2_{ajusted}$
	$HHV = 0.1343[C] - 1.5021[H] - 0.0027([O]^2/(1 - [Ash]/100)) + 29.1328(1 - [Ash]/100)$				Not $R^2_{ajusted}$
	$HHV = 0.2798[C] - 0.8491[H] + 0.7249[O] - 0.0092([O]^2/(1 - [Ash]/100)) - 0.1185[S]$				Not $R^2_{ajusted}$
	$HHV = 0.328[C] + 1.419[H] + 0.0928[S] + 0.2767([O] + [N]) + 0.1104[Ash] - 14.2783$				Not $R^2_{ajusted}$
	$HHV = 0.6610(0.328[C] + 1.419[H] + 0.0928[S]) + 0.1465([O] + [N]) - 0.0314[Ash]$				Not $R^2_{ajusted}$
	$HHV = 0.6838(0.328[C] + 1.419[H]) + 0.0000928[S] - 0.0000238[N] + 0.1546[O] - 0.0331[Ash]$				Not $R^2_{ajusted}$
Callejón-Ferre et al.	$HHV = -1.563 - 0.0251[Ash] + 0.475[C] - 0.385[H] + 0.102[N]$	Greenhouse crop residues: courgette (*Cucurbita pepo* L.), cucumber (*Cucumis sativus* L.), aubergine (*Solanum melongena* L.), tomato (*Solanum lycopersicum* L.), bean (*Phaseoulus vulgaris* L.), pepper (*Capsicum annuum* L.), water melon (*Citrillus vulgaris* Schrad.) and melon (*Cucumis melo* L.).	2011	[8,9]	
	$HHV = -0.465 - 0.0342[Ash] - 0.019[VM] + 0.0483[C] - 0.388[H] + 0.124[N]$				
	$HHV = -0.603 - 0.033[Ash] - 0.019[VM] + 0.0485[C] - 0.380[H] + 0.124[N] + 0.030[S]$				
	$HHV = -1.642 - 0.024[Ash] + 0.475[C{+}N] - 0.376[H{+}N]$				
	$HHV = -0.417 - 0.012[VM] - 0.035[A] + [C] + 0.518[C{+}N] - 0.393[H{+}N]$				
	$HHV = 9.756 - 309.454[VM]^{-1} + 6.164[H]^{-1} + 0.006[C]^2$				
	$HHV = 4.622 + 7.912[H]^{-1} - 0.001[Ash]^2 + 0.006[C] + 0.018[N]^2$				
	$HHV = 23.668 - 7.032[H] + 0.002[Ash]^2 + 0.005[C]^2 + 0.771[H]^2 + 0.019[N]^2$				
	$HHV = 86.191 - 2.051[Ash] - 1.781[C] + 237.722[Ash]^{-1} + 0.030[Ash]^2 + 0.025[C]^2 + 0.026[N]^2$				
	$HHV = 8.725 + 0.0007[Ash^2H] + 0.0004[VM^2H] + 0.0002[C^2N] - 0.014[H^2Ash] + 0.626[S^2Ash] - 3.692[S^2N]$				
	$HHV = 101.450 - 2.197[Ash] + 0.0282[C]^2 + 0.172[Ash + N] - 2.156[VM + N] - 230.927[C{+}N] + 0.029[C{+}S]$				

C: carbon (wt% dry basis); H: hydrogen (wt% dry basis); N: nitrogen (wt% dry basis); S: sulphur (wt% dry basis); O: oxygen (wt% dry basis); FC: fixed carbon (wt% dry basis); VM: volatile matter (wt% dry basis); Ash (wt% dry basis); Not $R^2_{ajusted}$: lack of $R^2_{ajusted}$ in multivariate model. MSW: municipal solid waste.

Table 5
Recent models based on structural composition.

Researcher	Correlation (HHV, MJ kg^{-1} dry basis)	Biomass types	Publication year	References	Comments
Shafizadeh and Degroot	HHV = 0.17389[Ce] + 0.26629[L] + 0.32187[E]	Lignocellulose materials	1976	[158]	References with errors
Tillman	HHV = 0.17389[Ce] + 0.26629(100 − [Ce*])	Wood	1978	[142]	References with errors
White	HHV = 17.9017 + 0.07444[L*] + 0.0661[E][a]	Wood (with extractives)	1984	[111]	Not R^2_{ajusted}, No SE
	HHV = 17.6132 + 0.0853[L*][a]	Extractive-free wood			Not R^2_{ajusted}, No SE
	HHV = 17.4458 + 0.0907[L*][a]	Extractive-free softwood			Not R^2_{ajusted}, No SE
	HHV = 18.0831 + 0.0637[L*][a]	Extractive-free hardwood			Not R^2_{ajusted}, No SE
	HHV = 17.7481 + 0.0800[L*](100 − [E])/100 + 0.0886[E][a]	Wood (with extractives)			Not R^2_{ajusted}, No SE
Jiménez and González	HHV = (1 − [Ash]/([Ce] + [L] + [E]))(0.17389[Ce] + 0.26629[L] + 0.32187[E])	Wheat Straw, olive twigs, olive wood, vine shoots, sunflower stalks, cotton plant stalks, sunflower seed husks, olive stones, olive marc, holm oak residues, eucalyptus residues.	1991	[156]	Not R^2_{ajusted}, No SE
Demirbaş	HHV** = 0.0889[L**] + 16.8218	Wood and non-wood	2001	[112]	No SE
	HHV** = 0.0893[L**] + 16.9742	Wood: beech wood, hardwood, *Ailanthus* wood, softwood, spruce wood, wood bark.			No SE
	HHV** = 0.0877[L**] + 16.4951	Non-wood: tobacco leaf, corn cobs, corn straw, wheat straw, waste material, tobacco stalk, hazelnut shells, olive cake			No SE References with errors
Demirbaş	ΔHHV = $0.00639[E]^2$ + 0.223[E] + 0.691	Spruce trunkwood, spruce trunk bark, beech trunk wood, beech trunk bark, *Ailanthus* trunk wood, sunflower shells, almond Shells, hazelnut shells, olive husks, hazelnut kernel husks, walnut shells	2002	[104]	No SE References with errors
Demirbaş	HHV** = 0.0864[L**] + 16.6922	Sunflower shells, almond shells, hazelnut shells, wood bark, olive husks, hazelnut kernel husks, walnut shells	2003	[110]	No SE
Demirbaş	ΔHHV = 0.383[E] − 0.0387	Hazelnut shells, wheat straw, olive husks, beech wood, spruce wood, corn cobs, tea waste, walnut shells, almond shells, sunflower shells	2004	[18]	Not R^2, No SE

Ce: cellulose (cellulose and hemicelluloses) (wt% dry basis); L: lignin (wt% dry basis); E: extractive matter (wt% dry basis); * indicates composition in % by mass on dry, and extractive-free basis; ** indicates composition in wt% on dry ash/extractive-free basis. No SE: no study of errors; Not R^2: lack of R^2 in univariate model; Not R^2_{ajusted}: lack of R^2_{ajusted} in multivariate model.

[a] Correlations converted to Mj kg^{-1} with the following conversion factor: 1 Btu lb^{-1} = 2.3261×10^{-3} Mj kg^{-1}.

In 1991, Jiménez and González [156] proposed a more complete model than those described above, which took into account the contents of cellulose + hemicellulose, lignin, extractives and ash.

Lignin was the most commonly used variable by Demirbaş in his models based on the results of structural analysis. In 2001 [112] this author proposed three models (on a dry ash/extractive-free basis), one for use with biomass in general, the others for use with wood and non-wood materials. These models, especially the general model, have been often cited [18,24,36,37,41,104], sometimes with small errors [110] or without stating the basis on which the results are provided [139].

In 2002, Demirbaş proposed a model [104] for predicting ΔHHV, in this case a quadratic equation involving extractives (dry basis) which was applicable to biomass in general. It has been cited on some occasions [37,41,139].

In 2003, Demirbaş [110] proposed another model similar to that of 2001. This was cited by Hernández Moreno in the following year [139]. Finally, in 2004, Demirbaş [18] proposed a model for determining the HHV with reference to the content of extractives which was applicable to a wide range of biomass materials.

4.5. Models based on the analysis of physical properties

Certain physical properties, such as viscosity (μ) and density (d) have been used in models to predict the HHV. Naturally, these models are only applicable to liquid biomass material, e.g., vegetable oils (Table 6).

Demirbaş et al. [146] studied the density of vegetable oils, alcohols and alkanes, and proposed a linear model for each. This equation for vegetable oils has been transcribed by other authors [36,37,41,139,159], but with the larger coefficient values; no explanation of why they should be larger was given. A year later, Demirbaş [159] proposed two new models involving density (d), one quadratic and the other cubic, but with an algebraic expression missing from the second. In addition, the correlation coefficient for this second equation appears absurd, suggesting a typographic error has been made. In the same article, this author proposes three other equations involving the variable viscosity (μ). Among these, the linear equation for μ has been cited by other authors [37,41,139]. In 2008, Demirbaş [160] proposed a further development of this model, and presented a relationship between μ and d. In the same paper this author also contemplated the flashpoint as a predictive variable, but only for biodiesel.

The latest model based on the physical properties of biomass was proposed by Sadrameli et al. [157], which relates the d of fatty acids to their HHV.

4.6. Models based on the results of chemical analysis

Table 7 shows the models for calculating HHV based on the results of chemical analysis. In 1982, Goering et al. [161] proposed a model relating the HHV of vegetable oils to the mean number of carbon atoms and double bonds in fatty acids. This equation, however, has only been cited once by another author [162].

Demirbaş [162] also studied the chemical composition of vegetable oils with respect to their aptitude as fuels, referring to their saponification values (SV) and iodine index (IV). This model has been referred to on several occasions [4,36], sometimes with errors [37,41,139].

In 2006, Demirbaş [36] proposed another model relating the number of double bonds in the fatty acids of vegetable oils with the latters' HHV. Three years later [43] the same author related the yield of liquid distillate to the HHV. Meanwhile, Sadrameli et al. [157] proposed two models for fatty acids, one requiring knowledge

Table 6
Recent models based on physical properties.

Researcher	Correlation (HHV, $MJ\,kg^{-1}$)	Biomass types	Publication year	References	Comments
Demirbaş et al.	$HHV = 79.014 - 43.126[d]$	Vegetable oils: safflower seeds, *Crambe*, corn, rapeseed, soybean, safflower seeds, cotton seeds, sunflower seeds, linseed, castor	1999	[146,159]	No SE
Demirbaş	$HHV = -45.736 + 224.028[d] - 142.935[d]^2$ $HHV = 229.006 - 664.213[d] + 813.29[d]^2 - 343.476\,[d]^3$ $HHV = 37.945 + 0.0491[\mu]$ $HHV = 38.934 - 1.836 \times 10^{-3}[\mu] + 6.252 \times 10^{-4}[\mu]^2$ $HHV = 29.696 + 0.732[\mu] - 0.0183[\mu]^2 + 1.58 \times 10^{-4}[\mu]^3$	Vegetable oils: linseed, olive, safflower seeds, soybean, corn, rapeseed, beechnut, *Crambe*	2000	[159]	No SE No SE Fixed error No SE No SE No SE
Demirbaş	$HHV = 0.0317[\mu] + 38.053$	Vegetable oils: *Ailanthus*, bay laurel, beech, beechnut, corn, cotton seed, *Crambe*, hazelnut, linseed, mustard oil, olive, palm, peanuts, poppy seeds, rapeseed, safflower seeds, safflower, sesame, soybean, spruce, sunflower seeds, walnut	2008	[160]	No SE
Sadrameli et al.	$HHV = -93.4[d] + 122.67$	Fatty acid: butanoic, pentanoic, hexanoic, heptanoic, octanoic, decanoic, lauric, palmitic, stearic, oleic, linoleic, linolenic	2008	[157]	No SE

d: density ($g\,cm^{-3}$); μ: viscosity ($mm^2\,s^{-1}$); No SE: no study of errors.

Table 7
Recent models based on chemical composition.

Researcher	Correlation (HHV, MJ kg^{-1})	Biomass types	Publication year	References	Comments
Goering et al.	HHV = 33.74 + 0.3356[WACL] − 0.07946[WADB]^2	Vegetable oils: castor, corn, cottonseed, *Crambe*, linseed, peanut, rapeseed, safflower, sesame, soybean, sunflower	1982	[161]	No SE
Demirbaş	HHV = 49.43 − (0.041[SV] + 0.015[IV])	Vegetable oils: *Ailanthus*, bay laurel, beech, beechnut, corn, cottonseed, *Crambe*, hazelnut kernels, linseed, peanut, poppy seeds, rapeseed, safflower seed, safflower, sesame, soybean, spruce, sunflower seeds, walnut kernels	1998	[162]	Not R^2_{ajusted}, No SE References with errors
Demirbaş	HHV = 40.35 − (0.64[DB$_1$] + 1.30[DB$_2$]) + 1.92[DB$_3$])	Vegetable oils	2006	[36]	Not R^2_{ajusted}, No SE
Sadrameli et al.	HHV = 0.0518[Mw] + 29.76 HHV = 0.7271[CN] + 31.419	Fatty acid: butanoic, pentanoic, hexanoic, heptanoic, octanoic, decanoic, lauric, palmitic, stearic, oleic, linoleic, linolenic	2008	[157]	No SE
Demirbaş	HHV = −0.0687[*D*] + 45.161	Vegetable oils and animal fats: corn, cotton seed, hazelnut kernel, linseed, peanuts, rapeseed, sesame, soybean, sunflower seed, tallow	2009	[43]	No SE

Mw: molecular weight; CN: carbon number; *D*: yield of distilled liquid (DAF). WACL: weighted average number of carbon atoms in the fatty acid chains; WADB: weighted average number of double bonds in the fatty acids; SV: saponification value (mg KOH/g oil); IV: iodine value (g I/100 g oil); DB$_1$: "content (wt%) of a one number of double bond" according to the original author; DB$_2$: "content (wt%) of a two number of double bond" according to the original author; DB$_3$: "content (wt%) of a three number of double bond" according to the original author. It is not clear what DB$_1$, DB$_2$ and DB$_3$ mean in the original texts. No SE: no study of errors; Not R^2: lack of R^2 in univariate model; Not R^2_{ajusted}: lack of R^2_{ajusted} in multivariate model.

of the molecular weight, the other knowledge of the number of C atoms.

4.7. Models based on other variables

In 1991, Khan and Abu-Gharah [163] proposed a model for the obtention of the HHV of domestic refuse via knowledge of its proportions of food waste, paper and cardboard, plastics, rubber materials and leather. The Conventional [128,130] and Tokyo models [164] are similar.

5. Conclusions

Biomass is a renewable energy resource that will likely be much more exploited in the near future. Not only will it help to provide needed energy, its carbon neutrality makes it attractive as a means of preventing further man-made climate change.

The thermochemical treatment of biomass, especially its direct combustion, is the most commonly used method for extracting its energy. This is usually measured in terms of HHV or LHV. The determination of the HV is very expensive since it requires the use of specialised equipment. In the industrial setting it would also delay the use of a biomass as a fuel. However, the HHV and LHV can be measured using models based on the results of relatively simple analyses, e.g., proximal, elemental, structural physical or chemical analysis.

Over the 20th century, the results of elemental analysis have been extensively used to develop models to predict the HV of coal, although in the last 30 years they have also been used to develop models for use with biomass. All have taken into account the C content since this has a direct impact on the HV. In many models it is the only variable that needs to be known. Other models also take into account the H and O contents, the N and S contents, or other elements. The models with simpler algebraic equations, or the greatest range of application, are those most commonly cited in the literature. Their results are usually expressed on a dry basis. However, few researchers have centred their studies on particular types of biomass, preferring to focus on models of more general use.

Models based on the results of proximal analysis have traditionally been less important, although from the mid 1980s researchers have underscored their economic benefits and ease of use. Of the three variables involved in this type of model, the FC is obtained by the difference between the total weight and the percentage weights of VM + ash. However, since the values of these variables are inter-related, such models are mathematically questionable. As for models based on the results of elemental analysis, the simplest, and those of most general application, have received most interest.

Some models involve the results of both elemental and proximal analysis, usually expressed in terms of the weight percentages of different elements and ash.

A smaller number of models produced over the last 35 years have involved the results of structural analysis. These generally relate the HHV to the lignin content of biomass, or the content of extractives. The cellulose content was used in earlier models of this type. Although some such general models have been proposed, they more commonly refer specifically to wood or other types of biomass. The simplest of these models have attracted the most interest.

More recent models have been proposed involving the variables d and μ, largely by a single researcher. These involve one or other of these variables and their use is limited to liquid biofuels (mostly vegetable oils).

Models relying on the results of chemical analysis have focused on obtaining the HHV of vegetable oils and some animal fats. Other

types of model have also been proposed, but have received little attention.

This review highlights the errors and deficiencies detected in the published models, as well as the frequent failure to provide the data on which they were developed, the lack of information about the basis used (dry basis or DAF basis etc.), the use of non-SI units, and the errors made the transcription and referencing of models by other authors. The large number of errors observed is of concern. Researchers should take care to detect those that have crept into the literature and try to prevent their continued reproduction.

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